STUDY OF CORROSION PERFORMANCE OF ZINC COATED STEEL IN SEAWATER ENVIRONMENT

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ABSTRACT

In this study, the corrosion protective mechanisms of zinc coating for mild steel in seawater were examined using weight loss, and electrochemical impedance spectroscopy methods (EIS). Coating is a technique to control the corrosion of a metal by providing an impervious metallic barrier by using sacrificial anode. The samples used in this study were fully zinc coated steel, zinc coated steel with scratch and mild steel as a control. Each sample undergoes the immersion process in seawater for 40 days. The results showed the corrosion rate of fully zinc coated steel decreases with immersion time from 0.03 mm/y to 0.01 mm/y and for zinc coated with scratch, from 0.034 mm/y to 0.012 mm/y. Impedance measurements studies revealed that fully zinc coated steel behave predominantly to be more practical anode in applying a great protection barrier for mild steel.

***Keywords**:* Coating, Mild steel, Seawater

NOMENCLATURE

electrode microscope *WE* working electrode
w_o initial weight g
w_L weight loss g
w_i final weight g
FRA Frequency response analyzer
GPES General purpose electrochemical
EIS Electrochemical impedance spectroscopy
AC Alternating current
CE Counter electrode
SCE saturated calomel electrode *SEM* scanning

1. INTRODUCTION

Corrosion is the chemical reaction between a metal by chemical or electrochemical reactions with its environment. Mild steel is used in large amounts in marine application because it offers excellent mechanical properties and lower cost. The study of mild steel corrosion phenomena in seawater has become a great challenge for corrosion engineers or scientists nowadays [1-3].

The use of coatings usually metal coatings is applied to protect other metal by dipping, electroplating, spraying, cladding, and diffusion [4-6]. Some of the applications for utilize the coating method for providing a good protection layer to the metal is depends on several aspects, including the type of metal to be protected, lifetime and type of coated material and environmental consideration. All coating provides barrier protection; that is they provide barrier between corrosive environment and the metals. The basic concept of coating is the more active metal undergoes corrosion and the less active metal is protected from the corrosion.

Zinc, like all metals, corrodes when exposed to the atmosphere. However, because of its ability to protect other base steel, it becomes the primary anti – corrosion component which used as a sacrificial anode in marine environment especially in ship, hulls, offshore oil and gas and underground pipelines [7-8]. This coating material offers lower price compare to other metallic coatings such as tin, chromium, nickel, or aluminium and it is an infinitely recyclable material. Zinc ions dissolved predominantly from the zinc coating form the surrounding barrier of corrosion products at the defect, thereby protecting the exposed iron.

Hot dipped galvanizing, also known as general galvanizing, is an acknowledged process for produce a quality zinc coating by completely immersing the steel product in a bath of molten zinc. It is the most commonly used method of applying metallic coatings to atmospherically exposed steel or in fresh and salt water applications [9].

In the present investigation, the corrosion behaviour of mild steel was evaluated in seawater using weight loss method, and electrochemical impedance spectroscopy (EIS). Besides, the surface morphology analysis using scanning electron microscope (SEM) was also determined.

2. METHODOLOGY

2.1 Materials

36 pieces of mild steel coupons were cut into 35mm x 25mm x 3mm used for immersion test. The specimens were polished successively using 600, 800, and 1200

gritted emery papers. Next, the polished specimen were degreased with acetone to remove any oxides from the surface and rinsed with distilled water before and after the experiment. 24 of the specimens were sent to Hot-Dip Galvanizing for coating by using the method of hot-dipping. 12 out of 24 zinc coated steel specimens were scratched by using saw.

2.2 Weight Loss Measurement

The rectangular mild steel specimens were immersed in 20 liter of seawater and hung in the aquarium for 40 days. Before exposure to the aggressive medium, the samples were cleaned with acetone and weighed for the original weight (w_0). The weight loss of mild steel specimens was determined after 10 days time intervals of immersion. The corroded specimens were cleaned by immersed it in sulfuric acid solution for about 2-3 minutes. Then the specimens were cleaned with distilled water and dried. The weight loss of the sample was determined by using Equation (1):

$$w_l = w_o - w_i \quad (1)$$

where w_o and w_i is the initial weight and final weight respectively.

The rates of corrosion of samples were determined by using Equation (2):

$$C_R \text{ (mm/y)} = 87.6 \text{ x } \left(\frac{W}{DAT} \right.$$

where W is weight loss, D is density of sample A is total surface area, and T is time of exposure to seawater.

2.3 Electrochemical Impedance Spectroscopy

The unit of electrochemical measurement apparatus was set up by combination of mild steel coupon as working electrode (WE), platinum sheet counter electrode (CE) and a saturated calomel electrode (SCE) in a cell. The electrodes were arranged in contact with the 150mL of electrolyte. The measurement was conducted using frequency response analyzer (FRA), an instrument which determines the frequency response of a measured system. A small amplitude AC signal will be imposed by FRA to the fuel cell via the load [10]. All of impedance parameters were recorded over a scanning rate of $8 mVs^{-1}$. This measurement is carried out at frequency range of 1 KHz – 0.1 Hz.

3. RESULT AND DISCUSSION

3.1 Weight Loss Measurement

Figure 1 ilustrates the results of the weight loss of specimen in tropical seawater with different feature of mild steel surface immersed in seawater for 40 days. It has been observed that the weight loss of the samples in all cases increased with increasing of immersion time. The control specimen indicated the higher weight loss compares to other specimen coated with zinc. This behavior could be attributed to the unprotected layer over the surface against the corrosion attack. The formation of red rust which is the corrosion product over the mild steel is due to the dissolution mechanisms when immersed in aggressive medium.

It is also found that the best corrosion resistance was experienced for the mild steel which fully zinc coated. The weight of steel shows the declination at the end of immersion test due to the corrosion process over zinc layer. Zinc anode corroded because of the differences in electrical potential between the metals and electrolyte and the corrosion products tends to fill the pores providing consistent cathodic protection.

Nevertheless, it can be seen that the shape of curve of mild steel with or without scratch at zinc coating showed only a few differences. Such behavior is happened because of the existance of zinc coating which created a great barrier effect to the steel eventhough the inhomogeneities of layer due to appearance scratch over the steel surface.

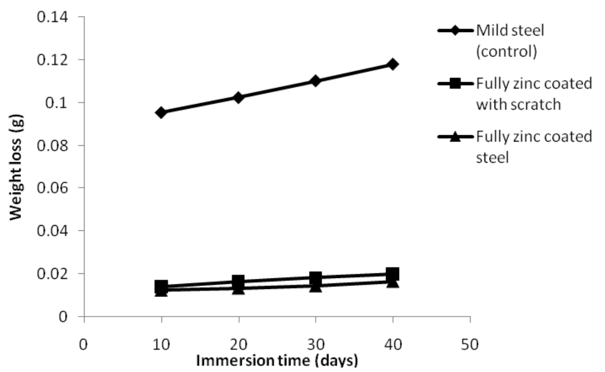

Figure 1 Weight loss versus immersion time in seawater mild steel with different surface treatments

The effect of applying zinc rich plate over the mild steel can seen from Table 1, the corrosion rate of control specimen indicates the higher values compared to other mild steel protected with sacrificial anode. While, the corrosion rate of fully zinc coated steel is relatively more stable and lower than fully zinc coated steel with scratch. Means, the bare steel was strongly damages due to the exposure to the seawater as no protection existed.

Table 1 Corrosion parameters obtained from weight loss measurement of mild steel in seawater with different surface treatments

Sample	Days	Weight loss (g)	Corrosion rate (mm/y)
mild steel (control)	10	0.0953	0.21
	20	0.1023	0.113
	30	0.1102	0.081
	40	0.118	0.065
fully zinc coated steel with scratch	10	0.0141	0.034
	20	0.0166	0.02
	30	0.0183	0.015
	40	0.0201	0.012
fully zinc coated steel	10	0.0124	0.03
	20	0.0134	0.016
	30	0.0145	0.012
	40	0.0166	0.01

3.2 Electrochemical Impedance Spectroscopy

AC impedance experiment for mild steel corrosion in seawater was carried out and the corrosion parameters were recorded. The impedance diagram produces by this system was examined have almost a semicircular appearance. As seen in Figure 2, it shows a capacitance loop in the high frequency (HF) range and an inductive loop in low frequency (LF) range. The result revealed that the zinc coating behaved as a physical barrier interface between the metal and the solution for blocking the electrochemical process occurs to the mild steel. Fully zinc coated steel indicates the higher protection or resistance to the corrosion compared to others due to the size of curve in complex plane. This behaviour is referred to the charge transfer reaction in the electric double layer formed between the metal surface and corrosive medium. CPE is the constant phase element which behaves like a double layer capacitance, C_{dl} and it controls the charge transfer process. A great protection film leads to the decreasing of CPE attributed to a decrease in local dielectric constant. Through the curve of bare mild steel (control), it is revealed the higher corrosion process occurr ed due to the adsorption of ions in the solution takes place on the metal surface without any blocking process. When this happen, the metal surface was suffered with the formation of rust or the corrosion product and had become even worse when it continues exposed to the seawater.

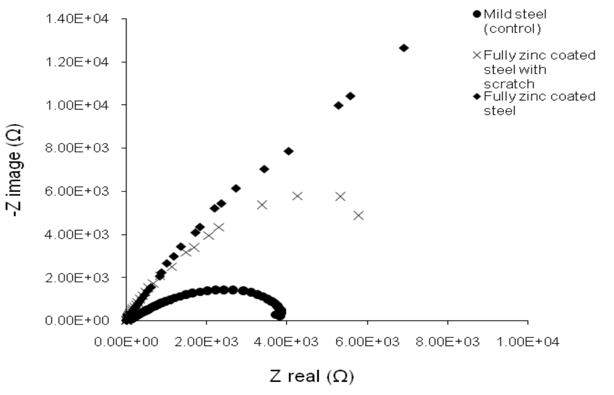

Figure 2 Complex plane for mild steel in seawater with different surface treatments

It clearly could be seen from the Table 2, the values of polarisation resistance, R_p is increased as the existence of zinc layer. The higher R_p value presents to a lower corrosion process of mild steel. However, the other coated specimen indicates lower R_p value compares to the fully zinc coated steel even though the surface is equipped with physical barrier. Such a phenomenon could be attributed to the existence of scratch over the coated material and the layer started to lose its stability to overcome the corrosion attack to the metal. The scratch over the coating layer contributed to the exposure to the ions in the solution. The exposed steel was found to corrode and forms a pocket of rust over the opening sections. This is referred as coating failure which can be occurred in the industry.

Table 2 Corrosion parameters obtained from impedance measurement of mild steel in seawater with different surface treatment

Sample	Rp (kΩ)	Cdl(µF)
mild steel (control)	4.1096	29.5505
fully zinc coated steel with scratch	6.4522	24.0366
fully zinc coated steel	7.1945	11.6431

3.3 Surface Morphology of Specimen

Polished mild steel specimen immersed in seawater in absence and presence of zinc coating were examined by using scanning electron microscope (SEM). The SEM micrograph reveals the presence of protective product film of zinc. Due to the formation of cracking over the bare mild steel in Figure 3a), it reveals that the surface was strongly damaged by the corrosion process. Untreated mild steel can be seen clearly the abundant of red dust over the surface compare to other metal covered with zinc. Figure 3b) and c) shows the mild steel specimen becomes significantly smooth surface even though inhomogeneities of zinc film over the specimen surface.

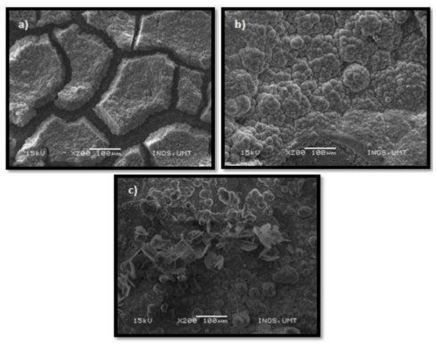

Figure 3 SEM morphology of a) untreated mild steel b) zinc coated steel with scratch and c) fully zinc coated steel at magnification of 200x

4. CONCLUSION

- Both mild steel coated with zinc act as a good protective film in seawater. Nevertheless, the fully zinc coated steel is best surface treatment compare to zinc coated steel with scratch due to the corrosion rate decrease from 0.030 mm/y to 0.010 mm/y and 0.034 mm/y to 0.012 mm/y, respectively.
- The EIS measurement proved that zinc coating act as a sacrificial anode in order to prevent underlying steel from corrosion. This is due to the higher value of corrosion resistance of mild steel covered by zinc rich plate.
- SEM analysis showed a good barrier effect on mild steel surface after being treated with zinc coating.

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REFERENCES

[1]. Ostovari, A., Hoseinieh, S.M., Peikari, M., Shadizadeh, S.R., and Hashemi, S.J. 2009. Corrosion inhibition of mild steel in 1M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawsone, Gallic acid, α- D Glucose and Tannin acid). Corrosion Science, 51, pp. 1935-1949

[2]. Hamdy, A.S., Sa'eh, A.G., Shoeib, M.A. and Barakat, Y. 2007. Evaluation of corrosion and erosion-corrosion resistances of mild steel in sulfide-containing NaCl aerated solutions. Electrochimica Acta, 52, pp. 7068-7074

[3]. M. Hazwan Husin, M. Jain Kassim, N.N. Razali, N.H Dahon and D. Nasshorudin. 2011. The effect of tinospora crispa extracts as a natural mild steel corrosion inhibitor in 1M HCl solution. Arabian Journal of Chemistry, pp.
1878-5352

[4]. Shibli, S.M.A., Jayalekshmi, A.C. and Remya, R. 2007. Electrochemical and structural characterization of mixed oxides-reinforced hot-dip zinc coating. Surface & coating Technology, 201, pp. 7560-7565

[5]. Yang Dong, Chen Jianshe, Han Qing, and Liu Kuiren. 2009. Effects of lanthanum addition of corrosion resistance of hot-dipped galvalume coating. Journal of Rare Earths, 27, pp. 114-118

[6]. Loto, C.A. and Popoola, A.P.I. 2011. Effect of anode and size variations on the cathodic protection of mild steel in seawater and sulphuric acid. International Journal of the Physical Sciences, 6, pp. 2861-2868

[7]. Marchebois, H., Joiret, S., Savall, C., Bernard, J. and Touzain, S. 2002. Characterization of zinc-rich powder coatings by EIS and Raman spectroscopy. Surface and Coating Technology, 157, pp. 151-161

[8]. Shibli, S.M.A and Sony George. 2007. Electrochemical impedance spectroscopic analysis of activation of Al-Zn alloy sacrificial anode by RuO_2 catalytic coating. Applied Surface Science, 253, pp. 7510-7515

[9]. Amadeh, A., Pahlevani, B., Heshmati- Manesh, S. 2002. Effects of rare earth metal addition on surface morphology
and corrosion resistance of hot-dipped zinc coating. Corrosion Science, 44, pp. 2321-2331

[10]. Lasia, A. 1999. Electrochemical impedance spectroscopy and its applications. 32, pp. 143-248